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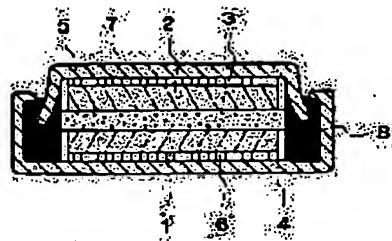
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(54) LITHIUM SECONDARY BATTERY

(57)Abstract:

PURPOSE: To increase discharge capacity and lengthen life by controlling pH of a positive active material having a specified composition to 10 or less.

CONSTITUTION: A positive active material is a composite oxide having layer structure or spinel structure represented by LiM_xO_y (M is at least one of Co, Ni, Mn, and Fe.), and whose pH is 10 or less. The active material is mixed with acetylene black and polytetrafluoroethylene powder in a weight ratio of 85:10:5, and toluene is added to the mixture, then they are kneaded, molded in a sheet, blanked in a disc, then heated under reduced pressure to obtain a positive electrode 1. The positive electrode is pressed against a positive can 4 through a current collector. A negative electrode 2 is formed by blanking a lithium foil in a disc, and pressed against a negative can 5 through a current collector. An electrolyte prepared by dissolving LiClO_4 in propylene carbonate is used. A lithium battery is assembled with the positive electrode 1, the negative electrode 2, the electrolyte, and a separator 3.



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CLAIMS

[Claim(s)]

[Claim 1] the lithium secondary battery characterized by being the lithium secondary battery which consists of a multiple oxide in which positive active material has the layer structure or Spinel structure given by LiM_xO_y (M -- one or more sorts of Co, nickel, Mn, or Fe -- containing .), and pH of said positive active material being ten or less.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the positive active material in more detail about a lithium secondary battery.

[0002]

[Description of the Prior Art] Recently, the cell which uses an organic baking object for a negative electrode for the active material which operating potential shows 4V order for the formation of a high energy consistency, or reinforcement is announced, and attention is attracted. Then, LiMO₂, such as lithium cobalt oxide and a lithium nickel oxide since it will say that a high energy consistency cell is hard to be obtained if the operating potential of a positive electrode is not high also when using an organic baking object for a negative electrode for reinforcement. The multiple oxide or LiM₂O₄ which has the layer structure shown. The multiple oxide which has the Spinel structure shown is proposed. These multiple oxides are compounded by calcinating them at an elevated temperature, using a carbonate, a hydroxide, a nitrate, etc. as a start raw material.

[0003]

[Problem(s) to be Solved by the Invention] if a lithium nickel oxide is taken for an example -- the composition -- as the source of nickel -- as nickel (OH)₂, NiCO₃, nickel (OH)₂, NiO, and the source of a lithium -- LiOH-H₂O, Li₂CO₃, and LiNO₂ etc. -- it is considering as the start raw material. Although obtained by mixing and calcinating these, dispersion was produced in discharge capacity by the handling under baking conditions or composition, and the stable cycle property was not acquired. this invention person used to be made in view of the above-mentioned trouble, and the place made into the purpose is to offer a long lasting lithium secondary battery with a large discharge capacity.

[0004]

[Means for Solving the Problem] in order to attain the above-mentioned purpose -- the lithium secondary battery of this invention -- positive active material -- LiM_xO_y (M -- one or more sorts of Co, nickel, Mn, or Fe -- containing.) x is 1<=x<=2, and y is the number of 2<=y<=4. It is the lithium secondary battery which consists of a multiple oxide with the layer structure or Spinel structure given, and said LiM_xO_y is characterized by pH being ten or less, and is characterized by being eight or less desirably.

[0005]

[Function] It turns out that the multiple oxide with the layer structure or Spinel structure given by LiM_xO_y has big effect on discharge capacity on the delicate conditions at the time of *****. As a result of examining this wholeheartedly, it turned out that it is greatly related to pH of the active material after baking. That is, if the unreacted source of a lithium remains at the time of baking, during actuation the inside of a furnace, and in atmospheric air, it will react with H₂O in air, and alkali, such as a lithium hydroxide, will be generated a front face or inside an active material. As for this, disassembly of the electrolytic solution is promoted with the alkali with which composition of an active material not only is not advancing completely, but remains. Consequently, while the capacity per unit weight decreases, resistance of a positive electrode goes up by the product produced by disassembly of the electrolytic solution, and it is thought that a cycle life falls. It is LiMO₂ making moisture management under composition severe, and by removing the produced alkali by rinsing etc. pH is made or less into ten and it becomes possible to offer a long lasting lithium secondary battery with a large discharge capacity.

[0006]

[Example] Hereafter, the example of this invention is explained below.

[0007] (Example 1) if in charge of preparation of a multiple oxide with the layer structure -- LiOH-H₂O and nickel (OH)₂ it uses and nickel atomic number is set to 1 by Li atomic number to 1 -- as -- weighing capacity -- it mixed, temporary baking was carried out at 420 degrees C among oxygen for 15 hours, and actual baking was carried out at 750 degrees C for 20 hours. The object which cooled in after [baking] dry air and was ground in the desiccation ambient atmosphere was used as positive active material.

[0008] The pH measurement of the compound positive active material was performed. It was 9.2, when injection churning of the 5g positive active material was carried out at 100ml distilled water and pH was measured. In addition, measurement of pH is JIS. It carried out based on K:5101. The same is said of the following examples and the example of a comparison.

[0009] The coin cell was made as an experiment as follows using this active material. An active material, acetylene black, and polytetrafluoroethylene powder were mixed by the weight ratio 85:10:5, toluene was added, and it kneaded enough. This was fabricated with a thickness of 0.8mm in the shape of a sheet with the roller press. next, this -- the diameter of 16mm -- it pierced circularly, and heat-treated at 200 degrees C under reduced pressure for 15 hours, and the positive electrode was obtained. The positive electrode was stuck by pressure and used for the positive-electrode can to which the charge collector was attached. The negative electrode pierced the lithium foil with a thickness of 0.3mm in a circle with a diameter of 15mm, and stuck by pressure and used it for the negative-electrode can through the charge collector. It is LiClO₄ to propylene carbonate. The fine porosity film made from polypropylene was used for the separator using the electrolytic solution which dissolved. one mol / . The with a diameter thickness [1.6mm thickness of 20mm] coin mold lithium cell was produced using the above-mentioned positive electrode, a negative electrode, the electrolytic solution, and a separator. This cell is set to A1. in addition, drawing 1 -- the sectional view of this invention cell -- it is -- 1 -- a positive electrode and 2 -- for a positive-electrode can and 5, as for a positive-electrode charge collector and 7, a negative-electrode can and 6 are [a negative electrode and 3 / a separator and 4 / a negative-electrode charge collector and 8] insulating packing.

[0010] (Example 1 of a comparison) While cooling in atmospheric air instead of cooling in after [baking] dry air, everything but grinding in atmospheric air produced the cell like the above-mentioned example 1 instead of grinding in a desiccation ambient atmosphere. pH of this positive active material was 12.0. This cell is set to B1.

[0011] (Example 2) Distilled water washed the active material produced in the above-mentioned example 1 of a comparison. This active material was used and also the cell was produced like the above-mentioned example 1. pH of this positive active material was 9.5. This cell is set to A2.

[0012] (Example 2 of a comparison) When calcinating, omitted temporary baking and only this baking was performed, and also the cell was produced like the above-mentioned example 1. pH of this positive active material was 10.7. Let this cell be B-2. Let this cell be B-2.

[0013] (Example 3) nickel₂ (OH) It is CoCO₃ to instead of. The cell was produced like the above-mentioned example 1 except using. pH of this positive active material was 7.9. Let this cell be A3.

[0014] (Example 4) nickel₂ (OH) It is CoCO₃ to instead of. The cell was produced like the above-mentioned example 1 except using what mixed FeO to 9:1 by the mole ratio. pH of this positive active material was 8.4. Let this cell be A4.

[0015] (Example 5) nickel₂ (OH) It is CoCO₃ to instead of. The cell was produced like the above-mentioned example 1 except using what mixed MnOOH to 9:1 by the mole ratio. pH of this positive active material was 8.4. Let this cell be A5.

[0016] (Example 6) if in charge of preparation of a multiple oxide with Spinel structure -- Li₂ CO₃ Mn 3O₄ it uses and Mn atomic number is set to 2 by Li atomic number to 1 -- as -- weighing capacity -- it mixed, temporary baking was carried out at 650 degrees C among atmospheric air for 6 hours, and actual baking was carried out at 850 degrees C for 24 hours. The object which cooled in after [baking] dry air and was ground in the desiccation ambient atmosphere was used as positive active material. The pH measurement of the compound positive active material was performed. pH of this positive active material was 9.5. The same cell as the above-mentioned example 1 was produced using this positive active material. This cell is set to A6.

[0017] (Example 3 of a comparison) While cooling in atmospheric air instead of cooling in after [baking] dry air, everything but grinding in atmospheric air produced the cell like the above-mentioned example 6 instead of

grinding in a desiccation ambient atmosphere. pH of this positive active material was 11.0. This cell is set to B3. Thus, the charge-and-discharge cycle trial was performed using the produced this invention cells A1 and A2, A3, A4, A5, A6 and the comparison cell B1, B-2, and B3. The test condition was set to 3mA of charging currents, charge termination electrical-potential-difference 4.2V, 3mA of discharge currents, and discharge-final-voltage 3.0V. The result is shown in drawing 2. The discharge capacity of this invention cell is superior to the comparison cell so that more clearly than drawing 2. Moreover, the relation between the capacity retention of each above-mentioned cell and pH is shown in drawing 3. Capacity retention was calculated by discharge capacity $\times 100$ of the discharge capacity / 1 cycle eye of a 100 cycle eye. The capacity retention of this invention cell is superior to the comparison cell so that more clearly than drawing 3.

[0018] In addition, this invention is not limited to the start raw material, the manufacture approach, a positive electrode, a negative electrode, an electrolyte, a separator, a cell configuration, etc. of the active material indicated by the above-mentioned example. Moreover, it is applicable to what uses an organic baking object for a negative electrode, an electrolyte, the thing which uses a solid electrolyte instead of a separator, etc.

[0019]

[Effect of the Invention] Since this invention is constituted like ****, the long lasting lithium secondary battery excellent in reversibility with a large discharge capacity can be offered.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view of the flat lithium secondary battery concerning the example 1 of this invention.

[Drawing 2] It is drawing showing the number of cycles and discharge capacity in a charge-and-discharge cycle trial.

[Drawing 3] It is drawing showing the capacity retention after the 100 cycles to pH of an active material.

[Description of Notations]

1 Positive Electrode

2 Negative Electrode

3 Separator

4 Positive-Electrode Can

5 Negative-Electrode Can

6 Positive-Electrode Charge Collector

7 Negative-Electrode Charge Collector

8 Insulating Packing

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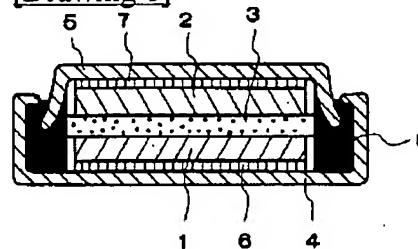
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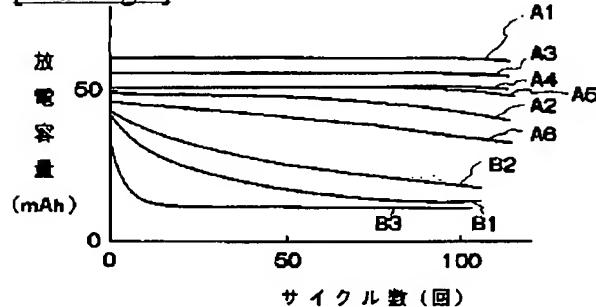
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DRAWINGS

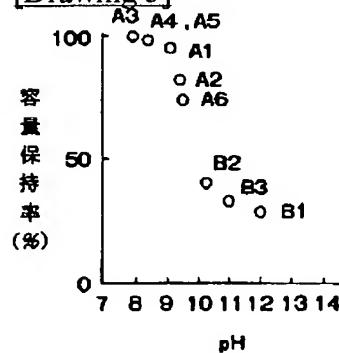
[Drawing 1]



[Drawing 2]



[Drawing 3]



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